

Canonical-grandcanonical ensemble in-equivalence in Fermi systems?

Dragoş-Victor Anghel

University of Oslo, Department of Physics, P.O. Box 1048 - Blindern, N-0316 Oslo, Norway.

(Dated: February 2, 2008)

I discuss the effects of fermionic condensation in systems of constant density of states. I show that the condensation leads to a correction of the chemical potential and of the Fermi distribution in canonical Fermi systems at low temperatures. This implies that the canonical and grandcanonical ensembles are not equivalent even for Fermi systems.

INTRODUCTION

Let a system \mathcal{S} be in contact with a heat and particle reservoir, \mathcal{R} . The microstates of the system will be denoted by m_i . If I assume that the system is ergodic and all the microstates corresponding to any fixed E and N are equally probable, then the probability associated to any state, say $p(m_{E,N})$ satisfies

$$p(m_{E,N}) \propto e^{\beta(E-\mu N)}, \quad (1)$$

where $\beta \equiv 1/(k_B T)$, T is the temperature, and μ is the chemical potential of the reservoir.

The same probability distribution may be obtained if we take as starting point information theory [1]. The information we start with is that the average energy and particle number are E and N , respectively. Then, the probability distribution (1) is the least biased estimate possible on the given information [1]. If the system is ergodic or not, is of no importance from this point of view. For a macroscopic system the maximum of the probability distribution is sharply peaked around the average values, $\langle N \rangle$ and $\langle E \rangle$, so both, particle number and internal energy, have well defined values.

Now let us assume that we can calculate (and measure) a macroscopic parameter, which I shall denote by X . The probability distribution over the microstates is given by Eq. (1) and from this one can calculate the probability distribution over the parameter X :

$$P_X(X) = \sum_i^{X(m_i)=X} p(m_i). \quad (2)$$

If X is well defined, then $P_X(X)$ should have a sharp peak at $X = \langle X \rangle$. If $P_X(X)$ has two maxims, then the system undergoes a phase transition. In each of the phases, one maximum dominates and this fixes the value of X for that phase [2, 3].

For a system of fermions a parameter which is surprisingly interesting to analyze is the number of particles that occupy completely an energy interval (no holes left in this interval), starting at the bottom of the single particle spectrum [3, 4, 5] – let me call this parameter N_0 and the energy interval $[0, \epsilon_0]$. In [3] I gave an example of an interacting system for which the probability distribution $P_{N_0}(N_0)$ forms, below a certain temperature, two

competing maxims. One maximum, which exists for any $T > 0$, is located at $N_0 = 0$ and the other appears at finite N_0 . At transition temperature the maximum centered at $N_0 > 0$ equals the maximum existent at $N_0 = 0$ and a first order phase transition occurs. Above transition temperature, since $P_{N_0}(N_0)$ is maximum at $N_0 = 0$, $\langle N_0 \rangle (\gtrsim 0)$ is microscopical. Below transition temperature $P(N_0)$ is maximum at $N_0 > 0$, so $\langle N_0 \rangle > 0$ is a macroscopic quantity. Due to the interaction, an energy gap is formed between the degenerate N_0 particles and the rest of the particles.

The same parameter may be analyzed for a system of ideal fermions. Assume that the density of states (DOS) has the general form $\sigma(\epsilon) = C\epsilon^s$, where C and s are constants. Now I require that N_0 particles form a degenerate subsystem on the first N_0 energy levels, and the first hole in the spectrum appears at energy ϵ_0 (or energy level $N_0 + 1$ – see Ref. [4] for details). Using again Eq. (2), I calculate $P_{N_0}(N_0)$ or $P_{\epsilon_0}(\epsilon_0)$. If \mathcal{Z} is the partition function of the system, and \mathcal{Z}_{N_0} is the number of configurations with the first hole appearing at $N_0 + 1$, then $P_{N_0}(N_0) = \mathcal{Z}_{N_0}/\mathcal{Z}$ and $P_{\epsilon_0}(\epsilon_0) = \sigma(\epsilon_0) \cdot P_{N_0}[N_0(\epsilon_0)]$. Since \mathcal{Z} is a constant, the extrema of P are found by solving $d\mathcal{Z}_{N_0}/dN_0 = 0$, or $d\mathcal{Z}_{\epsilon_0}/d\epsilon_0 = 0$. Even more convenient is to work with $\log \mathcal{Z}_{N_0}$, which is [4]

$$\begin{aligned} \log \mathcal{Z}_{N_0} = & \left[-\beta \left(C \frac{\epsilon_0^{s+2}}{s+2} - \epsilon_0 \right) + \beta \mu \left(C \frac{\epsilon_0^{s+1}}{s+1} - 1 \right) \right] \\ & + C \int_{\epsilon_0}^{\infty} d\epsilon \epsilon^s \log \left[1 + e^{-\beta(\epsilon-\mu)} \right]. \end{aligned} \quad (3)$$

Since $d\mathcal{Z}_{N_0}/dN_0 = (d\mathcal{Z}_{N_0}/d\epsilon_0) \cdot (d\epsilon_0/dN_0) = (d\mathcal{Z}_{N_0}/d\epsilon_0) \cdot \sigma^{-1}(\epsilon_0) = 0$ implies $d\mathcal{Z}_{N_0}/d\epsilon_0 = 0$, I calculate [4]

$$\frac{d \log \mathcal{Z}_{N_0}}{d\epsilon_0} = -C\epsilon_0^s \left\{ \log \left[1 + e^{\beta(\epsilon_0-\mu)} \right] - \frac{\beta}{C\epsilon_0^s} \right\} = 0. \quad (4)$$

If $s > 0$, $\log P$ has one and only one maximum at $\epsilon_0, N_0 > 0$, so for any macroscopic systems (i.e. large enough C) there will be a degenerate subsystem on the lowest energy levels at any temperature. If $s = 0$ (e.g. particles in a two dimensional flat potential or in a one-dimensional harmonic potential) there is a transition temperature, $T_{c,2D}$, below which the maximum of $P(N_0)$ moves from $N_0 = 0$ to $N_0 > 0$, i.e. a degenerate gas

forms. The degenerate gas may be put in correspondence with the Bose-Einstein condensate in a gas of bosons with similar spectrum [3, 4, 5, 6] and for simplicity I shall call it the *Fermi condensate* or the degenerate subsystem. The most interesting case seems to be $s < 0$, when $\log P$ has either only one maximum, at $N_0 = 0$, or two maxima, at $N_0 = 0$ and $N_0 > 0$. As the temperature decreases, the second maximum increases and becomes bigger than the maximum at $N_0 = 0$.

The rest of the article is organized as follows: in Section 2 I discuss in some detail the probability distribution $P_{N_0}(N_0)$ for the two-dimensional Fermi gas and calculate the relevant parameters of the Fermi condensate. In Section 3 I use in the standard way the grandcanonical formalism to calculate the thermodynamic quantities. In section 4 I compare the entropy obtained in section 3 to the entropy of the thermodynamically equivalent Bose gas and point out the miss-fit from the low temperatures range. The solution is suggested in section 5: in the canonical or microcanonical ensemble the condensate region should be considered separately and the Fermi distribution applies only in the *thermally active layer*, which is the energy interval above the condensate. The last section is reserved for conclusions.

FERMI CONDENSATION AT CONSTANT DENSITY OF STATES

For constant σ , Eq. (4) has a solution if and only if $\log[1 + e^{-\beta\mu}] < (\sigma k_B T)^{-1}$. Therefore, as in [4], I define the condensation temperature $T_{c,F}$ by the equation

$$\log[1 + e^{-\beta_{c,F}\mu}] = (\sigma k_B T_{c,F})^{-1}. \quad (5)$$

If I assume that in the temperature range of interest $\sigma k_B T \gg 1$ (i. e. I consider macroscopic systems), then also $\beta\mu \gg 1$, and the equation above may be written as

$$N \approx \sigma k_B T_{c,F} \log(\sigma k_B T_{c,F}). \quad (6)$$

In Eq. (6) I used the approximation $N \approx \sigma\mu$, valid at low temperatures (see further, Eq. 9). For $T < T_{c,F}$, $1 \gg \log[1 + e^{\beta(\epsilon_0 - \mu)}] \approx e^{\beta(\epsilon_0 - \mu)}$ and the solution of Eq. (4) may be approximated by

$$\epsilon_{0,max} = \mu - k_B T \log[\sigma k_B T]. \quad (7)$$

The particle number that is associated to $\epsilon_{0,max}$ is $N_{0,max} = \epsilon_{0,max}\sigma = \sigma\mu - \sigma k_B T \log[\sigma k_B T]$. The distribution (3) is not symmetric and $\langle N_0 \rangle < N_{0,max}$. In the low temperature limit, $\langle N_0 \rangle$ converges to $N_{0,max}$, but general, closed analytical expressions for $\langle N_0 \rangle$ seem difficult to find.

Let me denote $\langle \epsilon_0 \rangle \equiv \langle N_0 \rangle / \sigma$. In the next sections we shall see that in a canonical *finite* system we have to consider that all the energy levels from 0 to $\langle \epsilon_0 \rangle \lesssim$

$\epsilon_{0,max}$ are occupied, and the Fermi distribution applies only to the energy levels from $\langle \epsilon_0 \rangle$ up-wards. For this reason, as mentioned in the Introduction, I shall say that the particles in the energy interval above $\langle \epsilon_0 \rangle$ form the *thermally active layer*. Obviously, both $\langle \epsilon_0 \rangle$ and $\langle N_0 \rangle$ are subject to fluctuations. By comparing Eq. (7) or (4) with Eq. (5), we observe that T is the condensation temperature for the gas in the thermally active layer. The total number of particles in the system is then calculated as

$$\begin{aligned} N &= \langle N_0 \rangle + \int_{\langle \epsilon_0 \rangle + \sigma^{-1}}^{\infty} \frac{\sigma d\epsilon}{e^{\beta(\epsilon - \mu)} + 1} = \sigma\mu - 1 \\ &+ \sigma k_B T \log \left[1 + e^{\beta(\langle \epsilon_0 \rangle + \sigma^{-1} - \mu)} \right] \approx \sigma\mu - 1 \\ &+ \sigma k_B T e^{\beta(\langle \epsilon_0 \rangle + \sigma^{-1} - \mu)} \approx \sigma\mu + e^{\beta(\langle \epsilon_0 \rangle - \epsilon_{0,max} + \sigma^{-1})} \\ &- 1 \approx \sigma\mu + \beta(\langle \epsilon_0 \rangle - \epsilon_{0,max} + \sigma^{-1}) \\ &\approx \sigma\mu + \beta(\langle \epsilon_0 \rangle - \epsilon_{0,max}) + e^{\beta(\epsilon_{0,max} - \mu)} \equiv \sigma\epsilon_F, \quad (8) \end{aligned}$$

where ϵ_F is the Fermi energy and I used the fact that $\sigma k_B T e^{\beta(\epsilon_{0,max} - \mu)} = 1$ (Eq. 4 or 7).

In the grandcanonical ensemble, if we do not take into account the degenerate subsystem, the total particle number is

$$\tilde{N} = \sigma\mu + \sigma k_B T \log [1 + e^{-\beta\mu}]. \quad (9)$$

The Fermi energy, denoted in this case by $\tilde{\epsilon}_F$, is given by the equation $\tilde{N} = \sigma\tilde{\epsilon}_F$, so for $\beta\mu \gg 1$ we have

$$\tilde{\epsilon}_F \approx \mu + k_B T e^{-\beta\mu}. \quad (10)$$

GRANDCANONICAL FERMİ GAS

Under grandcanonical conditions, the entropy and internal energy of a Fermi gas have the expressions:

$$S = -\sigma k_B^2 T [2Li_2(-e^{\beta\mu}) + \beta\mu \log(1 + e^{\beta\mu})] \quad (11)$$

$$\text{and} \quad U = -(k_B T)^2 \sigma Li_2(-e^{\beta\mu}), \quad (12)$$

respectively. If we assume that different ensembles are equivalent, then we can use Eqs. (9) and (12) to express μ and T in terms of N and U and plug these expressions into S . The result should be the same. Vice-versa, calculating $T = (\partial S / \partial U)^{-1}$ and $-\mu/T = (\partial S / \partial N)^{-1}$, one should obtain the grandcanonical temperature and chemical potential.

To illustrate this change of variables, I shall express S (Eq. 11) in terms of U and N in the limit of low temperatures. In this limit $\beta\mu \gg 1$ and I can neglect $e^{-\beta\mu}$ from Eq. (9), retaining

$$N \approx \beta\mu. \quad (13)$$

On the other hand, using the expansion

$$Li_2(-e^{\beta\mu}) \approx -\frac{(\beta\mu)^2}{2} \left[1 + \frac{\pi^2}{3(\beta\mu)^2} \right] \quad (14)$$

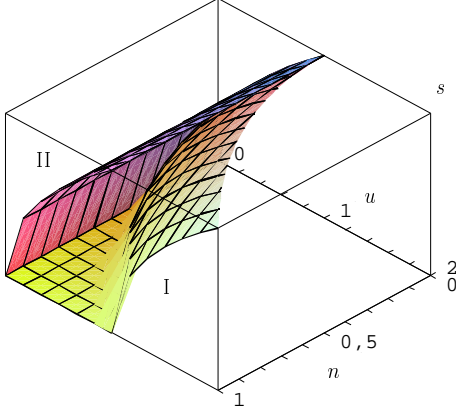


FIG. 1: Surface I: the entropy of a Fermi system, $s \equiv S/k_B\sigma$, as a function of $N \equiv N/\sigma$ and $u \equiv U/\sigma$. The range on the vertical axis is from 0 to $\pi\sqrt{2/3}$ (see Eq. 16). Surface II is obtained from surface I by subtracting from the energy U , the ground state energy of the system, $U_{g.s.}(N) = N^2/2\sigma$.

and Eq. (13), U may be approximated as

$$U \approx \frac{N^2}{2\sigma} \left[1 + \frac{\pi^2}{3} \cdot \left(\frac{\sigma k_B T}{N} \right)^2 \right]. \quad (15)$$

Eliminating $k_B T$ and $\beta\mu$ from Eqs. (13) and (15) plugging it into (11) I get

$$\frac{S}{k_B\sigma} \approx \pi \sqrt{\frac{2}{3} \cdot \left(\frac{U}{\sigma} - \frac{N^2}{2\sigma^2} \right)}. \quad (16)$$

The result (16) is plotted as surface I in Fig. 1.

Since $U_0(N) \equiv N^2/2\sigma$ is the zero temperature energy of the Fermi gas, let me denote the excitation energy by $U_B \equiv U - U_0(N)$ and define $S_B(U_B, N) \equiv S(U_B + U_0(N), N)$. A gas that has the internal energy U_B and entropy $S_B(U_B, N)$ as defined above, is called *thermodynamically equivalent* with the original Fermi gas (equivalence classes were defined in [3]). The chemical potential of the gas B is related to the chemical potential of the Fermi gas by $\mu_B = \mu - dU_0/dN = \mu - \epsilon_F$. In the low temperature limit

$$\frac{S_B}{k_B\sigma} \approx \pi \sqrt{\frac{2}{3} \cdot \frac{U_B}{\sigma}}, \quad (17)$$

which is plotted as surface II in Fig. 1. Another expression for U_B may be obtained by using Landen's relation, $Li_2(-y) + Li_2[y/(y+1)] = -\frac{1}{2} \log^2(1+y)$ [9, 12]:

$$U_B = (k_B T)^\sigma Li_2[(1 + e^{-\beta\mu})^{-1}]. \quad (18)$$

Applying Landen's relation to Eq. (11), I get

$$S = -\sigma k_B^2 T [2Li_2(-e^{\beta\mu}) + \beta\mu \log(1 + e^{\beta\mu})]. \quad (19)$$

THE EQUIVALENT BOSE GAS

It is well known that all the ideal gases of the same constant DOS and any exclusion statistics fall in the same equivalence class [3, 5, 8, 9, 10, 11]. Since the ground state energy of a Bose gas (energy at zero temperature) is zero, U_B defined in the previous section is nothing but the energy of the Bose gas and the surface II in Fig. 1 is the entropy of the Bose gas. From the bosonic perspective,

$$U_B = \int_0^\infty \frac{\sigma d\epsilon}{e^{\beta(\epsilon - \mu_B)} - 1} = \sigma (k_B T)^2 Li_2(e^{\beta\mu_B}). \quad (20)$$

and from Eqs. (20) and (18) I obtain $e^{-\beta\mu_B} = 1 + e^{-\beta\mu}$

In principle a macroscopic Bose gas of constant DOS does not condense, but in a finite system the ground state becomes macroscopically populated below a “condensation” temperature, $T_{c,B}$. The transition is not sharp, so $T_{c,B}$ may only be estimated. Grossmann and Holthaus [6] used the equation

$$N = \sigma k_B T_{c,B} \log N \quad (21)$$

as definition for $T_{c,B}$. Comparing $T_{c,B}$ with $T_{c,F}$, one can easily see that $T_{c,F} > T_{c,B}$, but they differ only by a factor $T_F/T_B = 1 + \log[\log(\sigma k_B T_{c,F})]/\log(\sigma k_B T_{c,F}) \gtrsim 1$.

Let me now examine closer the equivalence between the Bose and Fermi gasses below $T_{c,F}$. At these temperatures, the ground state population of the Bose gas is

$$N_0 = \frac{1}{e^{-\beta\mu_B} - 1} \approx (-\beta\mu_B)^{-1} = e^{\beta\mu} \approx \sigma k_B T_{c,F}, \quad (22)$$

which is of the order of N . In such a case the population of the ground state should be considered separately in all the equations. The total particle number in the Bose system should then be written as

$$N = N_0 + \int_{\sigma^{-1}}^\infty \frac{\sigma d\epsilon}{e^{\beta(\epsilon - \mu_B)} - 1} = N_0 + \sigma k_B T \log \left[1 - e^{\beta(\sigma^{-1} - \mu_B)} \right]. \quad (23)$$

Much below $T_{c,F}$, $\sigma\mu_B \ll 1$ and Eq. (23) may be approximated by

$$N - N_0 \approx \sigma k_B T \log(\sigma k_B T), \quad (24)$$

which is equivalent to Eq. (7).

Now a natural question arises: does the thermodynamic equivalence still holds at temperatures below condensation? For example at a temperature $T = T_{c,B}/2$, from Eq. (21) I get $\beta\mu \approx (2\sigma\mu/N) \log N \approx 2 \log N$, which, if plugged into the expression (22) for N_0 , gives

$$N_0 \approx e^{2 \log N} = N^2 \gg N! \quad (25)$$

One way to interpret this is that the thermodynamic equivalence breaks down at temperatures around and below $T_{c,F}$, i.e. when the population of the ground state

becomes macroscopic. Therefore, below $T_{c,F}$ the transformation $U \rightarrow U_B$ and $S \rightarrow S_B$, presented in the previous section, does not lead to the bosonic entropy. But this cannot be true, since it was shown that there exist a one-to-one correspondence between the microscopical configurations of a Bose and a Fermi system, of identical constant DOS and the same excitation energy [3, 11]. Therefore, the canonical entropies and partition functions ought to be the same. In this case, what do we have to tailor? The answer is: *the canonical partition function of the Fermi gas*.

CANONICAL FERMION GAS

By the exclusion statistics transformation (EST) method [3, 5] every distribution of fermions along the single particle energy axis is transformed into a distribution of bosons. The N_0 fermions that form the Fermi condensate are mapped onto bosons on the ground state (the Bose condensate). For a system of constant DOS the rest of the particles have a Fermi distribution and are mapped onto a Bose distribution of particles. This transformation have been made explicitly in Section V.A of Ref. [5]. The bosonic chemical potential is given by Eq. (23), with $N_0 \equiv \langle N_0 \rangle = (e^{-\beta\mu_B} - 1)^{-1}$. This fixes also the fermionic chemical potential to $\mu = \epsilon_F + \mu_B$ and the number of fermions in the condensate to $\langle N_0 \rangle$. As a consequence of this, in the limit of low temperatures $\beta(\epsilon_F - \mu)$ does not have the expected asymptotic behavior $\beta(\epsilon_F - \mu) \approx e^{-\beta\epsilon_F}$, but instead, from Eq. (23) I get

$$\begin{aligned} \beta(\epsilon_F - \mu) &= \beta\mu_B = [N - \sigma k_B T \log(\sigma k_B T)]^{-1} \\ &\approx \frac{1}{N} + \frac{\sigma k_B T \log(\sigma k_B T)}{N^2}. \end{aligned} \quad (26)$$

In addition, Jaynes' theory – according to which the probability associated to each microscopic configuration should have the form (1) – seems to contain intrinsic contradictions. The distribution (1) represents the least biased estimate given that the average number of particles in the system is N and the average energy is U . On the other hand, the bosonic distribution of the equivalent Bose gas is the least biased estimate, given the average *excitation energy* U_B and particle number N . As shown above, the two distributions *do not map onto each other over the whole spectrum*. In Ref. [5] it is proven that the situation is even more dramatic when the DOS is not constant.

CONCLUSIONS

In conclusion I discussed the effect of fermionic condensation – which is the apparition of a degenerate sub-

system at the bottom of the single particle spectrum – in a system of constant density of states. This leads to a correction in the calculation of the chemical potential in the canonical ensemble at low temperatures (see Eq. 26), which further implies that the canonical and grand-canonical ensembles are not equivalent at low temperatures even for Fermi systems.

By applying the exclusion statistics transformation to the Fermi system, one obtains a (thermodynamically equivalent [3]) Bose system. If the Fermi system is condensed, the degenerate subsystem is mapped onto the Bose-Einstein condensate – from where the name of Fermi condensate is derived. The condensate fluctuates and the value of these fluctuations are simply given by the condensate fluctuations of the equivalent Bose system. For the calculation of Bose ground state fluctuations in canonical and microcanonical ensembles I refer the reader to the articles of Holthaus et al. (e.g. [6, 14] and citations therein) and Tran et al. (e.g. [15] and citations therein).

Non-equivalence between grandcanonical Bose and Fermi gases have also been observed very recently by Patton et al. [16] in computer simulations of small systems.

-
- [1] E. T. Jaynes, Phys. Rev. **106**, 620 (1957); Phys. Rev. **108**, 171 (1957).
 - [2] K. Lee, Phys. Rev. E **53**, 6558 (1996); J. Lee and K.-C. Lee, Phys. Rev. E **62**, 4558 (2000).
 - [3] D. V. Anghel, J. Phys. A: Math. Gen. **35**, 7255-7267 (2002), cond-mat/0105089.
 - [4] D. V. Anghel, J. Phys. A: Math. Gen. **36**, L577(2003); cond-mat/0310248.
 - [5] D. V. Anghel, submitted to J. Math. Phys.; cond-mat/0310377.
 - [6] S. Grossmann and M. Holthaus, Phys. Rev. E **54**, 3495 (1996).
 - [7] B. DeMarco, S. B. Papp, and D. S. Jin, Phys. Rev. Lett. **86**, 5409 (2001).
 - [8] R. M. May, Phys. Rev. **135**, A1515 (1964).
 - [9] M. H. Lee, Phys. Rev. E **55**, 1518-1520 (1997).
 - [10] M. Apostol, Phys. Rev. E **56**, 4854 (1997).
 - [11] M. Crescimanno, and A. S. Landsberg, Phys. Rev. A **63**, 35601 (2001); cond-mat/0003020.
 - [12] L. Lewin, *Dilogarithms and associated functions* (McDonald, London, 1958).
 - [13] M. H. Lee, J. Math. Phys. **36**, 1217 (1995).
 - [14] M. Holthaus and E. Kalinowski, Ann. Phys. (N.Y.) **276**, 321 (1999).
 - [15] M. N. Tran, J. Phys. A, Math. Gen. **36**, 961 (2003).
 - [16] K. R. Patton, M. R. Geller, and M. P. Blencowe, cond-mat/0406285.